On the Origin of Colour in Paramagnetic Salts and Solutions

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I have to thank the members of the Indian Physical Society for electing me your President. I have been officially connected with the Society since its foundation in 1935, and it is an honour which I greatly appreciate being asked to preside over the affairs of the Society. I regret very much that pressure of other work prevents me from coming down to Madras and attend this annual meeting of our Society.

You have before you the report presented by the Council on the work of the Society during the past year. We have reason to congratulate ourselves on the satisfactory progress we have achieved during the five years of our existence, but we are aware that there is room for further improvement, in increasing the membership of the Society and also in making the latter more adequately represent the interests and activities of the physicists in India. The Council invite your suggestions and co-operation in achieving this aim.

Mention has been made in the annual report of the very interesting lecture on Cosmic Ray which Prof. Millikan gave before a meeting of the Indian Physical Society. We cordially welcome the presence of the distinguished physicist and his co-workers to this country, and we look forward to a very successful outcome of the investigations undertaken by them here.

The visit of these scientists to India, has raised in our minds the question of the possibility of locally initiating Cosmic Ray investigation in this country. India is surrounded by high mountains, and it will not be difficult to install permanent observation stations at altitudes up to 14,000 ft., which are not very far from centres of electrical and mechanical power supply. Further the extended land area and the favourable meteorological conditions during certain parts of the year, make this country specially suitable for balloon flight investigation. The Indian Meteorological Department is giving valuable assistance to Prof. Millikan and his party in their-investigations, and we hope later on the same help will be available to Indian physicists when they take up this line of work. Scientific

workers in India have made valuable contributions to the sciences of geodesy, meteorology and recently to our knowledge of the ionosphere. We look forward to a time when equally important contributions will be made from this country to our knowledge of the Cosmic Ray phenomena.

It is customary at such annual gathering for your president to deliver an address on some topic selected by him. A certain amount of latitude is given to him, and after some hesitation I have decided to place before you a connected account of a subject in which I have been interested for several years, it is on the origin of colour in paramagnetic crystals and solutions. The reason for my hesitation is that the President of the Physics section of the Indian Science Congress, who is an authority on the subject of crystal magnetism will probably deal with the subject of crystal magnetism in his presidential address, and there may be some overlapping between the subject matter of his discourse and mine. Still I hope I may be able to present you with a different way of approaching the investigation of the crystalline field present in paramagnetic crystals and solutions, whose influence is felt in diverse subjects like paramagnetic susceptibily, anisotropy, paramagnetic rotation and even colour.

In my address I shall first discuss how the concept of a molecular field, which is of electrostatic origin, arose gradually from a study of paramagnetic susceptibility, then how an elegant analytic method of investigating this crystalline field was developed by Bethe, Van Vleck and his fellow workers. Next it will be shown how a test of the optical consequence of Van Vleck's theory was undertaken by a study of the band absorption in paramagnetic crystals and solutions. Such a study led to the proposal of an empirical formula which appears better to account for the Stark splitting responsible for the absorption bands in these paramagnetic substances A theoretical deduction of the empirical formula is given, which permits of a fairly approximate calculation of the number and frequencies of the absorption bands in terms of the known constants of the paramagnetic ion and of the associated dipole molecules.

The discovery of the law of temperature variation of paramagnetic susceptibility is due to Curie's investigation with oxygen, when it was found that

$$\chi = \frac{C}{T}\ ;\ \text{where } \chi \text{ is the molar susceptibility.}$$

The theoretical interpretation of this relation was given by Langevin, who assumed that each oxygen molecule was the seat of a permanent magnetic dipole of moment μ. Langevin found that in a not too intense magnetic field $\chi = \frac{N\mu^2}{3kT}$; if we further take into consideration the tempera-

ture independent susceptibility observed in many substances, which are partly of diamagnetic and partly of paramagnetic origin then

$$\chi = \frac{N\mu^2}{3kT} + N\alpha \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

Weiss investigated the temperature dependence of the paramagnetic susceptibility of crystals and solutions, and showed that over fairly large ranges of temperature the Curie law in the modified form $\chi = \frac{C}{T-\Delta}$ holds. Weiss interpreted the correction factor Δ as due to the presence of an inner magnetic field of molecular origin. It was Debye who first showed that this molecular field was most probably of electrostatic origin.

The next line of investigation which again pointed to the presence of this crystalline field began with the quantum theory interpretation of the origin of the magnetic moment μ of the ions. According to the quantum theory the magnetic moment of a free ion with inner quantum number j is $\mu = j\beta$ where $\beta = \frac{eh}{4\pi mc}$ is the Bohr's unit of magnetic moment. This value of μ is not a constant, but depends upon the state of excitation of the ion. If the energy difference between the ground and the excited states of the ion is large compared to kT then the ions at the temperature T are all in the ground state, and in a field of strength H the $2j+1$ fold state of degeneracy of the ion is removed, and the average moment of the ion is $\mu = \sqrt{j(j+1)}\,\beta$

This relation first deduced by Hund was well verified in the case of the ions of the rare earth elements, *viz.* the experimentally determined values of μ agreed well with those calculated from spectroscopic data. When the same formula was tried to account for the measured magnetic moments of the ions of the iron group of elements, there was a total lack of agreement. It was pointed out by me in 1927 that the magnetic moment of a large number of simple and complex compounds of the iron group of element could be explained on the assumption that the orbital moments of these ions were completely quenched by the interaction with its neighbouring atoms in solids and solutions, so that the spin moment of the ions were alone free to orient in a magnetic field.

This leads to the formula

$$\chi = \frac{4S(S+1)}{3kT} N\beta^2 \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

In deducing the formula the analogy of the quenching of the temperature -variation of dielectric polarisation on solidification, observed in polar liquids, was used.

The investigation of the mechanism of the quenching of the orbital moment of ions in paramagnetic crystals or rendering them partially ineffective was the starting point of a series of important communications by Van Vleck and his fellow workers.

Van Vleck's Theory.

We have seen that the $2j+1$ fold degeneracy of an ion is totally removed by an axial magnetic field. If the ion forms part of a crystal, then due to the regular arrangement of other ions and atoms round it, an electric field of a given symmetry acts on the ion and thereby either partially or totally removes the degeneracy of the orbital moment of the ion, depending upon the symmetry properties of the crystalline field. Thus a Stark effect separation of the degenerate state of the ground term of the paramagnetic ion is produced. On the magnitude and degree of this separation will depend the future behaviour of the paramagnetic crystal in a superposed magnetic field. If the separation is small compared to the multiplet separation of the ground term of the ion, and also to the latter's spin orbital coupling, the inner quantum number of the ion retains its significance and Hund's formula will fairly represent the temperature variation of the susceptibility of such crystals. This is the case with the rare earth crystals, in which the incomplete $4f$ shell responsible for the paramagnetism of the rare earth ion is inside the $5s,p$ octet shell; the latter shields the former more or less effectively from the outer crystalline field.

In the case of the salts of the iron group of elements the $3d$ shell is the carrier of the paramagnetic effect and is fully exposed to the crystalline field. If the potential energy of the latter is large compared to the energy of the spin orbital coupling $\lambda(LS)$, then the latter breaks down and a Stark effect splitting of the L moment of the ion takes place, since an electric field has no direct effect on the spin moment.

Bethe in 1929 published an important investigation on the Stark splitting of the ground term of ions with S, P, D, F orbital quantum numbers. For example in a field of cubic symmetry the D term is split up into two components Γ_3 and Γ_5 the former is doubly degenerate and non magnetic, and the latter triply degenerate. The F term is split into three components Γ_2, Γ_5 and Γ_4 of which Γ_2 is non degenerate and non magnetic, while the two others are both triply degenerate. In a rhombic field, all the degeneracies of the ground term are completely removed. In a magnetic field, the spin and orbital moment of the ion will, upto the factor of spin orbital coupling, be free to orient independently—the orbital moment so far as its degeneracy has not been removed by the crystalline

field. Many of the paramagnetic salts like chrome alum belong to the cubic system, while in the case of others belonging to the hydrated crystals of the rare earth group, it is found that it is sufficient to take a predominantly cubic field. Such a field is however not capable of accounting for the observed paramagnetic anisotropy of the hydrated crystals containing Fe^{++}, Co^{++}, Ni^{++} and Cu^{++} ions. Penney and Schlapp suppose that an additional field of rhombic symmetry of low intensity is superposed on the dominant cubic field in these hydrated crystals. While in the case of certain other paramagnetic Alums Van Vleck has assumed the existence of a small trigonal field. The most general expression for the energy of an ion in a superposed crystalline and magnetic field of strength H is :

$$V = \Sigma[D(x_i^4 + y_i^4 + z_i^4) + Ax_i^2 + By_i^2 - (A+B)z_i^2]$$
$$+ \lambda_i(L.\ S) + \beta H(L + 2S) \quad \cdots \quad \cdots \quad (3)$$

where x_i y_i and z_i represent the coordinates of an electron in the d-shell of the ion, and the summation is over all the electrons present in the latter. The first term represents the dominant cubic field, the second represents the rhombic field, λ is the constant of the spin orbit interaction.

Fig 1. gives the term levels for the D and F ions.

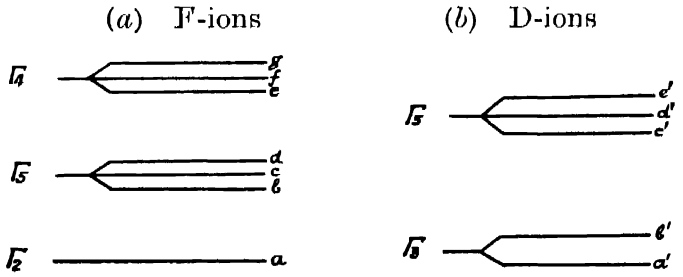

FIG. 1

(Upright in Ni^{++}, inverted in Co^{++}) (Upright in Cu^{++}, inverted in Fe^{++})

We shall first consider the conditions under which a paramagnetic crystal will have a spin only value for its susceptibility. They are :

(i) the ground term is non degenerate and non magnetic like Γ_2 of F

(ii) the crystalline field is essentially cubic

(iii) the distance between the ground and the upper terms is very large compared to kT.

(iv) the spin orbital coupling is negligible and

(v) the magnetic moment induced in the ground state a by the higher energy states like k which is of the form $2H\sum_k \frac{|\mu(ak)|^2}{h.\nu(ka)}$ is negligible.

Chrome alum is found to be magnetically isotropic with a magnetic susceptibility almost perfectly represented by formula (2). Penney and Schlapp find that the susceptibility is better represented by the formula $\chi = \frac{15N\beta^2}{3kT}\left(1-\frac{2\lambda}{5Dq}\right)^2$; the correction term represents the effect of spin orbital interaction.

Next we consider the case of the Nickel salts. Their susceptibility eg. of the hydrated sulphate is greater than the spin only value, and its magnetic anisotropy is about 30 per cent. Here it is assumed that the term sequence is the same as that in the chromic salts, only the separation is less, and there is a small rhombic field. In this case the induced magnetic moment due to the interaction with the triplet terms of Γ'_5 and Γ_4 are comparatively large, and we have a temperature independent susceptibility which is dependent upon the direction of the magnetic axis. Therefore the value of the induced moment is different along the three magnetic axes of the crystal, and this is the origin of the anisotropy of Nickel salts.

Penney and Schlapp have calculated the splitting of the F term in the cubic field and obtained the following values of the 3 Stark terms 0, 8 Dq and 18Dq where q is the multiplicative factor of D in equation (3) for a system of n electrons.

The value of $\bar{\chi}$ the mean susceptibility of Ni^{++} is found to be

$$\chi = \frac{8N\beta^2}{3kT}\left[1+\left(\frac{8\lambda}{3}-kT\right)(\alpha_1+\alpha_2+\alpha_3)\right]$$

where α_1, α_2, and α_3 are certain constants, proportional to the intensities of the rhombic field along the three magnetic axes.

Comparison of this expression after certain simplications, with the magnetic data enables the values of Dq to be calculated, which comes out to be 1485 cm^{-1} for Ni^{++} salts and 3730 cm^{-1} for Cr^{+++}. A knowledge of these constants enables us to calculate the Stark term separation for the F ion, they come out to be of the order of $10^4 cm^{-1}$.

Now Co^{++} (d^7 ^4F) has the same orbital term as Ni^{++} (d^8 ^3F) and carry the same ionic charge, but they differ greatly in their magnetic properties, viz. the susceptibility of Co^{++} shows a very large deviation from the Bose Stoner value, and the anisotropy of hydrated cobalt sulphate crystal is about 70%. Van Vleck shows that from theoretical consideration the term level in Co^{++} is inverse to that in Ni^{++} so that the ground term in the former is the triply degenerate Γ'_4 with a residual orbital moment. The contribution of the latter accounts for the larger deviation from the

spin only value of susceptibility in cobalt salts. Assuming the existnce of rhombic field, T'_4 is split up into three sub levels, and then the large anisotropy in Cobalt salts can at least be qualitatively interpreted.

So far nothing has been said of the way in which the triply degenerate T'_4 and T_5 levels can be split up. We find that more detailed specification is necessary to account for the spin only values of the paramagnetic susceptibilities of the alums of Vanadium and Titanium. This is only possible if the ground terms of both these ions are non degenerate and also non magnetic.

In Table I are given the various D and F ions and how they split up into upright or inverted terms in a cubic field according to Van Vleck's classification. The general principle underlying this tabulation appears to be that pairs of ions with the same orbital quantum number, the sum total of whose d electrons are either 5, 10, or 15 have opposite sequences of term.

According to this Table the ground term of Ti^{+++} is $d^1\ ^2D\ T'_5$ and of V^{+++} is $d^2\ ^3F\ T'_4$ both of which are triply degenerate; and as such their magnetic susceptibilities ought to deviate largely from the spin only values.

TABLE I.

Ions with D-term :		*Ions with F-term*	
Ion.	Theoretical.*	Ion.	Theoretical*
Ti^{+++}	Inverted	V^{+++}	Inverted
Cr^{+++}	Upright	Cr^{++++}	Upright
Fe^{++}	Inverted	Ni^{++}	do
Cu^{++}	Upright	Co^{++}	Inverted
$(MoO)^{+++}$	Inverted		
$(WO)^{++}$	do		
Ce^{+++}	do		

To account for the spin only value of magnetic susceptibility of these alums the following assumptions are necessary.

(i) that in these alums a field of lower symmetry than cubic exists in which the triply degenerate ground term T_5 and T'_4 are split up. This assumption was not necessary in the case of Chrome alum since the lowest level in Cr^{+++} is the non degenerate T'_2.

(ii) that in both cases the lowest of these terms is non-magnetic. If the lowest term is non-degenerate but has an orbital moment, then in the expression for magnetic susceptibility a term independent of temperature is added.

* As given by Van Vleck.

1. Van Vleck shows that in the alums an additional field of trigonal symmetry exists, which arises as shown by X-ray analysis from the fact that the principal axes of the unit cell round each paramagnetic ion do not coincide with the principal axes of the octahedral arrangement of the six associated water molecules. The Stark splitting in a trigonal field of Γ_4 and Γ_5 term is shown in fig. 2.

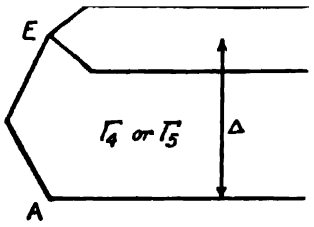

FIG. 2

(The splitting of a triply degenerate cubic state in a trigonal field. The two components of E coincide unless magnetic forces are applied).

2. Siegert has shown that in the most general type of trigonal field it cannot be expected that the non degenerate orbital level will be the deepest both for Ti^{+++} and V^{+++}. Under some special type of potential function for a trigonal field will this arise.

The general formula of the alums is $AMe(SO_4)_3$, $12H_2O$ where A is an alkali atom, Me is a trivalent atom. In the paramagnetic alums each paramagnetic ion is embodied in an octahedral arrangement of six water molecules, round which the SO_4 ions, the remaining H_2O molecules and the alkali atoms are grouped.

Van Vleck assumes that the cubic part of the field arises from the action of the six oriented dipole water molecules round each paramagnetic ion. Penney, Schlapp and others have calculated the value of Dq for the paramagnetic ions Cr^{+++}, Ni^{++}, Cu^{++}, the value is found to vary from 1480 to 3730 cm^{-1}. Van Vleck assumes a reasonable value $Dq = 1500$ cm^{-1}, and from it he finds that the dipole moment of the oriented water molecules. In this theory the effect of the polarisation of these molecules due to the charge on the paramagnetic ions plays no part.

From calculations made by Penney and Schlapp, in a cubic field a F ion is split up into three Stark levels with separations $8Dq$ and $18Dq$ for the upright ions like Cr^{+++} and Ni^{++} and $10\,Dq$ and $18Dq$ for inverted ions like Co^{++}, while for a D-ion like Cu^{++} the separation between Γ_3 and Γ_5 is $10Dq$.

Having obtained a clue of the origin of the cubic part of the crystalline field, Van Vleck proceeds to evaluate the splitting of the doubly

degenerate Γ_3 and the triply degenerate terms Γ_4 and Γ_5 in the trigonal field. According to him the latter arises from

(i) the direct action of the distant atoms *i.e.*, those beyond the six associated water molecules

(ii) the indirect action of these distant atoms on the associated water molecules, the latter become somewhat disturbed from their normal octahedral arrangement

(iii) the Jahn-Teller effect—which states that the most stable arrangement of a polyatomic molecule is always sufficiently unsymmetrical to lift the orbital degeneracy which may be present in the central atom.

Calculations made by Van Vleck show that the total splitting produced by this trigonal field is for V^{+++} ion (I'_4 term) from 460—860 cm^{-1} and the Ti^{+++} ion (I'_5 term) from 1450—2200 cm^{-1}, according to the special assupmtions made.

Optical Test of Van Vleck's theory.

In fig. 3 is given the energy diagram of the Stark splitting of the D and F ions due to a combined cubic and trigonal fields as present in the paramagnetic alums. It will be seen that in all hydrated paramagnetic

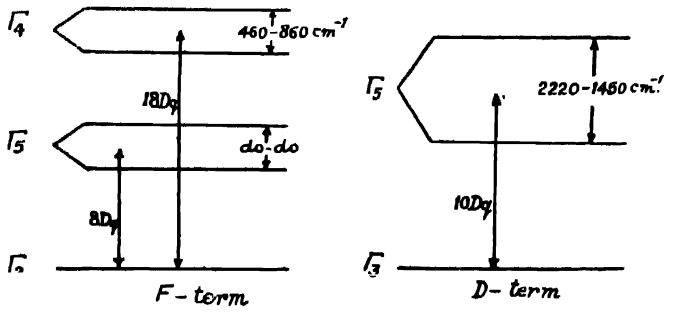

FIG. 3

Dq ~ 1500 cm^{-1} according to Van Vleck

crystals the separation between the Stark levels is of the order of 10^4 cm^{-1} ; transitions between them will produce absorption and emission spectra lying between the infra red and ultra violet regions and as such can be capable of optical verification. Another consequence of the theory is that according as the Stark levels of the ions are upright or inverted the highest absorption bands will show a doublet structure or a singlet structure. The latter will be a little complicated by the superposition of the spin orbital coupling. This will be specially noticeable in the absorption spectra due to Co^{++} and Ni^{++} ions. The investigation of the optical consequences of Van Vleck's theory has been undertaken by P. C.

Mukherji and myself[1])[2]), the results of which are given in two papers recently published. The conclusions drawn by us are that (i) Van Vleck's theory is unable to represent the number and frequencies of the principal absorption bands ; (ii) on the other hand the doublet separation shown by some of these bands agree fairly well with predictions made by Van Vleck for the paramagnetic alums ; (iii) the structure of the absorption bands to a large extent do not conform to the classification by Van Vleck into upright and inverted Stark levels. In the first paper[1]) we have proposed an empirical formula which appears to us to give a better representation of the number and frequencies of these absorption bands, and we have discussed the assumptions on which such a formula could be based. In a subsequent paper[3]) I have attempted a theoretical deduction of this formula.

Before proceeding further it will be desirable at this stage to say a few words about the general nature of the absorption bands shown by hydrated paramagnetic crystals and solutions. Most of them are coloured, with one or two absorption bands in the visible part of the spectrum. In those crystals and solutions whose infra red absorption spectra have been investigated like those of Nickel and Cobalt, we find absorption bands in the neighbourhood of 1.2μ. Some of the absorption spectra like that due to Cu^{++} show a single broad absorption band, others like that due to Ti^{+++} show a doublet structure. Under large dispersion the absorption bands due to Co^{++} and Ni^{++} ions appear to consist of a number of fine absorption bands. We shall for the present confine our attention to the mean frequencies of the broad absorption bands and of their prominent doublet structures.

The position of the absorption bands are dependent upon the nature of the solvent in which the crystals are dissolved, e.g. water, ammonia, alcohol, etc. It is assumed that in such solvents they form hydrated, ammoniated, alcoholated complexes, and the change in the position of the absorption bands in these solvents is to be attributed to the different strength of the crystalline fields which the associated water, ammonia, alcohol dipole molecules exert on the central paramagnetic ion. From a study of these principal absorption bands we find that the following empirical formula fairly represent their number and frequencies.

$$\Delta\nu = ne. \mid \Delta e_L \mid .C.P. \quad \ldots \quad \ldots \quad (4)$$

The assumptions underlying the above formula are that

(i) the ionic charge ne in a paramagnetic ion induces a polarisation proportional to P in the associated dipole molecules

(ii) in the electric field due to the polarisation of the dipole molecules, the paramagnetic ion which has an electric moment proportional to its orbital quantum number L, can occupy L+1 discrete energy levels each characterised by an electric quantum number e_L such that $o \leqq e_L \leqq L$

(iii) transitions between the ground term and the L upper levels will give rise to L absorption bands, whose frequencies are given by formula (4)

where C is a numerical constant

P, as we shall see later, is dependent both on the dipole moment μ and the polarisability γ of the associated dipoles.

Some of the consequences of this formula which can be verified are :

A. For the same kind of associated dipole molecules, e.g., water

(i) For the same ion the ratio of the absorption frequencies will be as 1 : 2 for D-ions

1 : 2 : 3 for F-ions

According to the theory of cubic splitting the frequency ratio will be for F ions either 8 : 18 or 10 : 18 according as the term sequence in the ion is upright or inverted.

(ii) For the D resp. F-ions, the separation of the corresponding bands in different ions will be as *nc* ; for doubly and triply charged ions the ratio will be as 2 : 3.

(iii) For the different ions

$$K' = ecP = \frac{\Delta \nu}{n.\Delta e_L}$$ ought to come out as a constant.

B. For the same ion associated with two different kinds of dipole molecules like water and ammonia, the ratio of their absorption frequencies will be proportional to their polarisability, i. e.,

$$\frac{\Delta \nu H_2O}{\Delta \nu NH_3} = \frac{P H_2O}{P NH_3}$$

In Tables II, III are collected the data for the known absorption bands due to paramagnetic ions with D and F orbital numbers. It will be seen that the conclusions (i) and (ii) are fairly verified, while the values of (e. C. P.) for D term varies between 2,580 to 3,380 cm $^{-1}$ with a mean value of 2,950 cm $^{-1}$ which is fairly good. For the F terms the agreement is not so good, the value of the constant varying from 2,640 to 4,130 cm^{-1}.

TABLE II.

Ions.	Configuration.	Ground term.	Selective Absorption. λ (A. U.)	ν (cm.$^{-1}$)	Centre of gravity (cm.$^{-1}$)	Transitions.	$K' = \frac{\Delta\nu}{N.\Delta eL}$.	Observers.
Ti^{+++}	$3d^1$	$^2D_{3/2}$	6100 5200	16,389 19,225	17,807	0—2	2.968 cm.$^{-1}$	Bose and Datta†.
$(MoO)^{+++}$ ...	$4d^1$	$^2D_{3/2}$	5800 5400	17,236 18,513	17.875	0—2	2,979 „	Kato §.
$(WO)^{+++}$.....	$5d^1$*	$^2D_{3/2}$	7000 6000	14,282 16,662	15,472	0—2	2,579 „	„
$(V.O)^{++}$.....	$3d^1$	$^2D_{3/2}$	7400	13,510	13,510	0—2	3,377 „	„
Cr^{++}	$3d^4$	$^5D_0$	7300— 6200 4500 4100	13,695— 16,125 22,216 24,388	14,910	0—2	3,423 „	„
Co^{+++}	$3d^6$	$^5D_4$	6120 4000	16,335 25,000	—	—	—	Topp ‖.
Fe^{++}	$3d^6$	$^5D_4$	10700 9500	9,343 10,523	9,933	C—2	2,483 „	Dreisch ¶.
Cu^{++}	$3d^9$	$^2D_{5/2}$	8200	12,192	12,192	2—0	3 064 „	Dreisch and Trommer**.
							Mean = 2,950 „	

* The doublet band is perhaps due to $Cr.^{+++}$

† This is discussed in detail later (see Table III).

‡ *Loc. cit.*

§ *Loc, cit.*

‖ Dissert. Münster (1928)

¶ *Zeits. f. Phys.* xl. p. 714 (1927).

** *Zeits. f. Phys. Chem* xxxvii. p. 37 (1937).

TABLE III

Ion.	Configuration.	Ground term.	Selective λ (A. U.)	Absorption ν (cm.$^{-1}$).	Centre of gravity (cm.$^{-1}$).	Ratio.	Transition.	$K' = \frac{\Delta\nu}{N.\ \Delta eL}$.	Observers.
V^{+++}	$3d^2$	$^3F_2$	6100	16,389	16,389	..	0—2	2,731 cm.$^{-1}$	Kato *.
			4200	23,803	23,803	2 : 3 ..	0—3	2,645 ,,	,,
V^{++}	$3d^3$	$^4F_{3/2}$	8200	12,192	12,620	..	0—2	3,155 ,,	,,
			7660	13,051		2 : 3			
			5600	17,852	18,180	..	0—3	3,055 ,,	,,
			5400	18,513					
Cr^{+++}	$3d^3$	$^4F_{3/2}$	6380	15,670	15,976	..	0—2	2,663 ,,	Datta and Deb †.
			6140	16,280		2 : 3			
			4470	22,365	22,807	..	0—3	2,667 ,,	Datta and Deb †.
			4300	23,249					
Co^{++}	$3d^7$	$^4F_{9/2}$	12500	8,000	8,000	..	..	.....	Dreisch ‡.
			7700	12,982	12,982	..	3—1	3,245 ,,	,, ‡.
			5150	19,413	19,413	2 : 3 ..	3—0	3,235 ,,	,, ‡.
Ni^{++}	$3d^8$	$^3F_4$	12100	8,262	8,262	..	0—1	4,131 ,,	Houstoun §.
			6870	14,552	14,552	1 : 2 ..	0—2	3,638 ,,	,,
			4050	24,684	24,684	2 : 3 ..	0—3	4,114 ,,	,,

* *Loc. cit.*
‡ *Zeits. f. Phys.* xl p. 714 (1927).
† *Loc. cit.*
§ Proc. Roy. Soc. Edin. xxxi. pp. 530, 538 (1910).

TABLE IV.

Ground state of the ion.	Substance.	Centres of selective absorption	Ratio $\frac{P_{NH_3}}{P_{H_2O}}$.
D-state	$CuSO_4{\cdot}5H_2O$	12,297 cm.$^{-1}$	
	$[Cu(NH_3)_4]Cl_2,H_2O$	14,160 ,,	
		Ratio..... ·87	
F-state	$[Cr(H_2O)_6]Cl_3$	18,200 cm.$^{-1}$, 24,100 cm.$^{-1}$	
	$[Cr(NH_3)_6]Cl_3$	21,500 ,, , 23,500 ,,	
		Ratio..... ·85 ·85	
	$[Ni(H_2O)_6]Cl_2$	8,497 cm.$^{-1}$, 15,370 cm.$^{-1}$, 25,510 cm.$^{-1}$	
	$[Ni(NH_3)_6]Cl_2$	10,804 ,, , 17,200 ,, , 27,900 ,,	
		Ratio..·79 ·89 ·91	
G. or H state	$[Co(H_2O)_6]Cl_3$	16,340 cm.$^{-1}$, 25,000 cm.$^{-1}$	
	$[Co(NH_3)_6]Cl_3$	19,460 ,, , 28,650 ,,	
		Ratio..... ·84 ·87	

In Table IV is given the ratio of the frequencies of absorption of the same ion when associated with water and ammonia dipoles. The value of this ratio varies between ·79 to ·91, while according to the theoretical formula to be deduced later this ratio is ·78 for D terms and ·74 for F terms (see p. 15, formula (6)). We may consider the agreement as fairly satisfactory.

We shall now briefly indicate the theoretical deduction of the empirical formula given above. It is assumed that round each paramagnetic ion six dipole molecules are completely oriented, occupying the six faces of a cube at distances $R = 2A^\circ$. The intensity of the field at the centres of these molecules is $E = \frac{nc}{R^2}$. Under the action of this field, the axis of each of the dipoles will point towards the ion, and also a polarisation γE will be induced on each of them. The combined effect of these two for each dipole will be a field of intensity F at the centre of the ion where

$$F = \frac{2\mu}{R^3} + \frac{2\gamma ne}{R^5}.$$

The resultant field due to the six oriented dipole molecules can be written as equal to CF. It is difficult to calculate the value of C ; we shall determine its value from experimental data. Apriori it can be seen that $C < 1$, due to the fact that the fields of the six dipoles acting on the central ion, will to a large measure neutralise each other. We assume that the ion has an electric moment M_L^E proportional to the orbital number L, and the

energy of orientation of the ion in the field of a single dipole molecule is taken to be

$$dW = M_L^E \cdot \frac{e_L}{L} \cdot C. F.$$

If the frequency of absorption due to a transition from the ground term is

$$\Delta\nu, \text{ then } \Delta\nu = \frac{\Delta W}{h} = -\frac{M_L^E}{L} \cdot |\Delta e_L| \cdot C. ne P \quad \cdots \quad \cdots \quad (5)$$

$$\text{where } P = \frac{2}{R^3 h}\left(\gamma + \frac{R^2}{ne} \cdot \mu\right)$$

From experimental data we find that $\frac{M_L^E}{L}$ is independent of L and we shall put $M_L^E = \bar{r} \cdot e \cdot L$, where r is the mean radius of the three quantum Hydrogen like ion with charge ne.

We shall determine the value of C from the absorption data for Ti^{+++} ion.

We take $n = 3$; $\bar{r} = 1{\cdot}08 \times 10^{-8}$ cm. approximately and it is found $F = 19.9 \times 10^5$

The calculated value of $\Delta\nu = C. 94.6 \times 10^3$ cm^{-1}

While the observed value = $17{\cdot}8 \times 10^3$ cm^{-1}.

So that, $C \sim \frac{1}{6}$ which appears to be quite plausible.

We shall next proceed to deduce a result of which we have previously made use, viz., we shall determine the ratio of the absorption frequencies, when the same paramagnetic ion has either water or ammonia molecules associated with it. The ratio comes,

$$\frac{\nu_{H_2O}}{\nu_{N_3H}} = \frac{\frac{2n_1\gamma_1 e}{R^5} + \frac{2\mu_1}{R^3}}{\frac{2n_2\gamma_2 e}{R^5} + \frac{2\mu_2}{R^3}} \quad \cdots \quad (6) \; ; \quad \begin{aligned} &\text{for water} && \mu_1 = 1.84 \times 10^{-18} \\ & && \gamma_1 = 1.49 \times 10^{-24} \\ &\text{for ammonia} && \mu_2 = 1.46 \times 10^{-18} \\ & && \gamma_2 = 2.26 \times 10^{-24} \end{aligned}$$

Taking $R = 2 \times 10^{-8}$ cms. the value of this ratio comes to be 0.78 for D ions and 0.74 for F ions (see p. 14 for verification).

I hope the above discussion will convince you that we have a fairly satisfactory basis for a theory of the origin of colour shown by hydrated paramagnetic salts and solutions. I will not overtax your attention by discussing the rough model on which I have made it plausible why the quantum number L is restricted between 0 and L and not between ± L.

It is useful at this stage to compare the two different methods of approach adopted by the school of Bethe and Van Vleck, and by the present writer. In the former from the consideration of symmetry an analytic expression for crystalline field which is suited to account for the paramagnetic phenomenon is deduced and by methods of group theory the number of Stark levels are calculated and their relative separation expressed in terms of an undetermined constant D. The latter is determined from the temperature variation of susceptibility or paramagnetic anisotropy of these crystals. Then by choosing a suitable mean value for this constant, it is found that the crystalline field is alone due to the dipole moment μ of the associated molecule. The effect of the central charge ne of the paramagnetic ion and the polarisability of the associated molecule play no part in the theory. This theory cannot, therefore, explain the greater frequencies of absorption in ammoniated as compared to the hydrated ion, since $\mu_{NH_3} < \mu_{H_2O}$, nor the dependence on the ionic charge. While in our method of approach we have started with the scrutiny of experimental data and shown how they can be best fitted to an empirical formula, of which a theoretical deduction is next attempted.

I next propose to show how the splitting of triply degenerate terms Γ_4 and Γ_5 in paramagnetic alums as calculated by Van Vleck can be experimentally verified.

Doublet structure of the bands—In Table V have been collected the doublet separation for the principal absorption bands for D and F ions. It will be noticed that the doublet separation lies within the limits calculated by Van Vleck for the splitting of the D and F terms. As some of

TABLE V.

D-term Ions.		F-term Ions.	
Ti^{+++}	−2886 cm.$^{-1}$	V^{++}	−859 cm.$^{-1}$
			659 ,,
Cr^{++}	−2430 ,,		
Fe^{++}	−1180 ,,	Cr^{+++}	−608 ,,
			874 ,,
$(MoO)^{+++}$	−1277 ,,	Co^{++}	−750 cm.$^{-1}$
$(WO)^{+++}$	−2380 ,,	Ni^{++}	no structure for the highest absorption band.
Ce^{+++}	−2408 ,,		

the data contained in the above tables are taken from absorption data for hydrated crystals and partly from paramagnetic solutions, we may conclude that some or all of the factors which according to Van Vleck produce the trigonal field in the alums are also effective in other hydrated crystals and solutions. Further discussion of these results are given in our second paper. Another interesting conclusion, which can be drawn from the fine structure of the absorption bands, is on the sequence of the Stark splitting in the ions responsible for them i.e. whether the splitting is upright or inverted.

In Table VI are collected the data of the Stark level sequences in different D and F ions as calculated by Van Vleck and as deduced from absorption data. It will be seen that in most of them Van Vleck's sequence

TABLE VI.

Ion.	Theoretical.*	Observed	Remarks.
Ions with D-term :			
Ti^{+++}	Inverted	Upright	Observed in HCl solution of $TiCl_3$, which may lead to an inversion of levels.
Cr^{++}	Upright	Upright	
Fe^{++}	Inverted	Upright	
Cu^{++}	Upright	Inverted	
$(MoO)^{+++}$	Inverted	Upright	
$(WO)^{++}$	do	do	Triplet observed due to the effect of large spin-orbital coupling.
Ce^{+++}	do	Inverted	
Ions with F-term :			
V^{+++}	Inverted	Upright	
Cr^{+++}	Upright	do	
Ni^{++}	do	Inverted	
Co^{++}	Inverted	Upright	

is not followed. The crucial case is the reversal of the sequences in Co^{++} and Ni^{++}, on which the whole theory of the large anisotropy of Co^{++} salts compared to that of Ni^{++} salts was based.

* As given by Van Vleck.

The point raised here is whether the interpretation of the origin of of the absorption bands, in hydrated paramagnetic crystals and solutions given above is valid ; also whether it is legitimate to apply the Stark level scheme deduced from it to the interpretation of paramagnetic anisotropy, and other magnetic properties.

I hope I may interest some of you to take up the study of light absorption in paramagnetic salts and solutions, specially with a view to the determination of the fine structure of the absorption bands. Many important problems as to the nature of the crystalline field in crystals and solutions await investigations, and can be attacked by the absorption spectra method.

References

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